Spin-unrestricted Geminals as Reference States in Electron Correlation Theory

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Abstract

To treat the electron correlation problem in molecules by multi-reference methods, we advocate for reference states constructed with two-electron functions (geminals) in their spin-unrestricted form. Geminal based reference functions should be corrected for the dynamical part of correlation, by means of perturbation theory, with or without, full or partial, spin restoration.

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1 Introduction

Replacing classical one-electron functions (molecular orbitals, MOs) by two-electron functions (geminals) aiming to improve the electronic structure description of molecules is an old idea[1–3]. It turned out soon that, while geminals can capture a significant part of static correlation, their energy is not sufficiently accurate to describe fine details of electronic structure. This is especially so if one applies the strong orthogonality (SO) condition[4], which represents an enormous simplification and leads to the method of antisymmetrized product of strongly orthogonal geminals (APSG)[5]. In its original form, APSG deals with singlet-coupled two-electron functions. It is well established

that APSG lacks a dominant part of dynamical correlation, and it is deficient in some static correlation scenarios as well, e.g. multiple-bond dissociation[6].

In our laboratory, we have long been using the APSG method as reference state[7–19]. The aim of this chapter is to review the family of methods, where the geminal-based wave function is not, or not fully singlet coupled.

Investigation of non singlet-coupled geminals was pioneered by Head-Gordon[20, 21] and Rassolov[22, 23]. Coming from Pople's group, they had ample experience with the classical spin-violating (or spin-relaxed) version of standard Hartree-Fock, dealing with one-electron functions. Exploring the gain in the performance by turning to spin-unrestriction for a wave function built with geminals was an obvious route of progress.

Below we recapitulate the benefits of using geminal wave functions, discussing the advantages of spin-contamination. We also consider spin restoration in order to get overall (exact or approximate) singlet or triplet electronic states for the entire molecule. Finally, perturbative correction schemes for recovering intergeminal correlation are considered.

An alternative strategy of generalizing APSG is to abandon the strong orthogonality restriction. The key acronyms here are AGP(Antisymmetrized Geminal Power)[24–29], APIG(Antisymmetrized Product of Interacting Geminals)[30, 31] or APG (Antisymmetrized Product of Geminals)[32, 33]. These theories are more powerful and also more complicated, especially APG, and will not be further discussed here. For some recent results, see e.g. Refs.[34–38].

2 Chemical significance of two-electron functions

The use of one-electron functions is ubiquitous in quantum chemistry. In the early days, it was for practical reasons that molecular orbital (MO) theory won over valence bond (VB) theory. While MO based approaches continue to be prevailing, VB has made comeback[39–41] and alternative theories also persist. Of the latter category one may mention

- numerical procedures where the many-electron wave function is represented on a grid;
- the "r_{12}"-schemes that use relative electron coordinates[1];
- density functional theories in their original (i.e. not Kohn-Sham) forms;
- density matrix functional theories (DMFT)[2];
- group function theories, that construct the entire $2N$-electron wave function by functions of n-electron with $2 \leq n < 2N$.

[1] Gaussian geminals represent a special "r_{12}" wavefunction class, different from the orbital-expansion based geminals discussed here.

[2] In the spirit of the present Volume, it is worth noting that there is a significant Hungarian contribution to the vast field of DMFT by Á. Nagy, see Ref.[42].

Geminals represent the $n = 2$ special case of group function theory. The fact that *electron pairs* are included, has special significance. At the beginning of his career, one of the present authors (PRS), had a seminar in Madrid on using geminals. During the discussion a well-known professor from the USA congratulated him and advised: "Carry on! Two-electron functions are better than one-electron functions. Then you go to three-, four-, etc.-electron functions. The higher, the better!"

PRS did not realize immediately, that the advice of the famous professor was not completely perfect. The point is that the description of many chemical systems is qualitatively correct at the level of self-consistent, one-electron MOs and two-electron geminals usually bring an improvement over this. The same does not necessarily hold when stepping to groups of more than two electrons. For example, one cannot properly describe the CH_4 molecule in terms of three-electron units without destroying its tetrahedral symmetry...

3 Hungarian contributions to the theory of geminals

Geminals were introduced in Hungarian quantum chemical circles in the early sixties of the 20th century, by Ede Kapuy, who performed intensive research in the subject[43–45]. His early papers discuss non-SO constructions for which he derived energy formulas. He later focused on the conceptually more simple, SO assumption. Some of his papers are still being cited (see e.g. [46]). When Kapuy's interest turned to many-body perturbation theory (MBPT) with localized MOs, he quit geminal theory.

In the 1970-s research with an expressed focus on geminals declined, though alternant molecular orbital theory and different orbitals for different spin construction remained active fields, and turned out to be geminal related, due to the underlying pair-function structure[47]. From the middle 80-s, Surján initiated extensive work in geminals[8–11, 48]. Several Hungarian quantum chemists, starting their career with Surján also contributed to the field, among others Kállay[13], Rosta[12], Szabados[17, 18, 49–51]. The end of the XXth century saw a revival of geminals at the international level too[22, 23, 52–62].

4 Motivations for using unrestricted geminals

Consider the geminal product wave function for a $2N$-electron system

$$\Psi \;=\; \psi_1^+ \psi_2^+ \cdots \psi_N^+ |\mathrm{vac}\rangle \;, \tag{1}$$

written with SO, $m_S = 0$ geminals expanded on the basis of orthonormal spatial orbitals φ_i as

$$\psi_\mu^+ \;=\; \sum_{ij \in \mu} C_{ij}^\mu \; \varphi_{i\alpha}^+ \varphi_{j\beta}^+ \;. \tag{2}$$

The Ansatz of Eq. (1) exhibits $M_S = 0$ from the point of view of total $\hat{S}_z$, correct S however (belonging to total $\hat{S}^2$) is obtained only in special cases. The simplest among these is singlet coupling, with all ψ_μ characterized by geminal spin $s = 0$. (Perfect pairing terminology is also in use for the singlet-coupled, SO geminals based product function[63].) The other, spin-pure possibility for Eq. (1) is $s = 1$ for one of the ψ_μ's and $s = 0$ for the rest, $N - 1$ geminals, giving overall $S = 1$. All other combinations of spin-pure or spin-mixed geminals result in a spin-contaminated overall function in the form of Eq. (1).

Symmetry of the coefficient matrix $\boldsymbol{C}^\mu$ reflects geminal spin in a simple manner, i.e.

1. if $C^\mu_{ij} = C^\mu_{ji}$, geminal μ is a pure singlet, $s = 0$;
2. if $C^\mu_{ij} = -C^\mu_{ji}$, geminal μ is a pure triplet, $s = 1$;
3. if $\boldsymbol{C}^\mu$ is neither symmetric nor antisymmetric, geminal μ is in a spin-contaminated (singlet-triplet mixed) state.

The singlet-coupled form of Eq. (1) corresponds to a Lewis-structure of the system and represents a good approximation of the ground state when one way of distributing singlet electron pairs in the molecule provides a reliable picture. By variational optimization of Eq. (1) one-electron orbitals in fact localize in space, and geminals μ can be directly attributed with the concept of bonding, non-bonding, core, lone etc. pairs. It has been observed at an early stage, that perfect pairing breaks down whenever multiple Lewis-structures are needed for a qualitatively correct description of the system[6]. Taking the classical example of the benzene molecule, singlet coupling with Eq. (1) provides two isoenergetic minima, corresponding to the two Kekulé structures. The problem has been approached from several angles, resulting e.g. restricted pairing[64], VB variants[40] or coupled-cluster VB[65] methods. A common feature of these workarounds is that a linear combination of terms corresponding to different Lewis-structures is explicitly included. Building blocks of the individual terms are typically spin-pure two-electron units and the correct overall spin is ensured by suitable coupling, following e.g. Rumer, Kotani or Serber[66]. To overcome the combinatorial growth of computational demand stemming from spin-coupling possibilities of all pairs, restrictions are introduced based on chemical intuition, hierarchical construction, etc.

Allowing geminals in Eq. (1) to become singlet-triplet mixed is a conceptually simpler way of achieving the same goal, i.e. incorporation of spin-couplings beyond all-singlet pairs. While computational complexity of such an approach essentially agrees with that of perfect pairing, spin-coupling of geminals remains flawed in general. This is only partly due to the absence of $m_S = \pm 1$ geminal states. Even if admitting high- and low-spin triplet geminals[67], the single product Ansatz is not flexible enough to recover various spin-couplings with proper, individual coefficients.

Spin-symmetry breaking Ansätze in the form of Eqs.(1)-(2) were explored by Head-Gordon and Rassolov, independently. Writing the geminal expansion with the help of unrestricted orbitals, they initially relied on both spatial and spin integration in fulfilling orthogonality of orbitals belonging to different geminal subsets[20, 52]. It was later found advantageous to introduce more restriction, ensuring SO only by the spatial

parts of the orbitals used for expanding the geminals[21, 22]. This latter form relates directly to unrestricted HF (UHF), when allowing two orbitals per geminals.

The connection of UHF to spin-mixed SO geminal Ansätze is rather straightforward, assuming that the spatial part of UHF orbitals are paired in Löwdin's sense[68, 69]. Orbitals ϕ_μ, associated with α spin and χ_ν, associated with β spin are considered paired when obeying

$$\langle \phi_\mu | \chi_\nu \rangle \;=\; \lambda_\mu \delta_{\mu\nu} \; . \tag{3}$$

They allow to express the UHF geminal as

$$\psi^+_{\mu,\mathrm{UHF}} \;=\; \phi^+_{\mu\alpha} \chi^+_{\mu\beta} \tag{4}$$

and $\psi_{\mu,\mathrm{UHF}}$ give rise to the UHF wavefunction when substituted in Eq. (1). As a consequence of Eq. (3), $\psi_{\mu,\mathrm{UHF}}$ in Eq. (4) is expanded in such a two-dimensional set of one-electron orbitals, that is orthogonal to the two-dimensional set of any index $\nu \neq \mu$. Relating the paired UHF orbitals to the orthogonal set of UHF natural orbitals (UNOs) as[70, 71]

$$\begin{aligned} \phi_\mu &= \cos(\alpha_\mu)\, \varphi_1 \;+\; \sin(\alpha_\mu)\, \varphi_2 \; , \\ \chi_\mu &= \cos(\alpha_\mu)\, \varphi_2 \;-\; \sin(\alpha_\mu)\, \varphi_2 \; , \end{aligned}$$

the UHF geminal of Eq. (4) can be recast in the form of Eq. (2) with the coefficient matrix reading as

$$\boldsymbol{C}^\mu_{\mathrm{UHF}} \;=\; \begin{pmatrix} \cos^2(\alpha_\mu) & -\sin(2\alpha_\mu)/2 \\ \sin(2\alpha_\mu)/2 & -\sin^2(\alpha_\mu) \end{pmatrix} \; . \tag{5}$$

Parameter α_μ is related to the diagonal of the interrelation overlap in Eq. (3) as $\lambda_\mu = \cos(2\alpha_\mu)$.

Since Eq. (5) involves a single parameter, UHF does not use all flexibility of the spin-unrestricted SO geminals' product Ansatz. A two-dimensional, normalized geminal coefficient matrix involves two independent variables in the general case, according to

$$\boldsymbol{C}^\mu \;=\; \begin{pmatrix} \cos(\gamma_\mu)\, \cos(\delta_\mu) & \sin(\delta_\mu)/\sqrt{2} \\ -\sin(\delta_\mu)/\sqrt{2} & -\sin(\gamma_\mu)\, \cos(\delta_\mu) \end{pmatrix} \; . \tag{6}$$

The role of parameters γ_μ, δ_μ in spin components and their mixing in geminal μ is discussed in Ref.[72]. Substituting $\delta_\mu = 0$ in Eq. (6) sets $\boldsymbol{C}^\mu$ symmetric, whereby ψ_μ is pure singlet. Antisymmetric $\boldsymbol{C}^\mu$, i.e. pure triplet geminal is obtained with $\delta_\mu = 90°$.

It can be easily checked that the spin-summed geminal density matrix $\boldsymbol{D}^\mu = \boldsymbol{C}^{\mu\dagger}\boldsymbol{C}^\mu + \boldsymbol{C}^\mu \boldsymbol{C}^{\mu\dagger}$ is diagonal, reflecting that Eq. (6) corresponds to natural orbitals. Occupation number of orbitals φ_1 and φ_2 read

$$\begin{aligned} D^\mu_{11} &= 2\cos^2(\delta_\mu)\, \cos^2(\gamma_\mu) \;+\; \sin^2(\delta_\mu) \; , \\ D^\mu_{22} &= 2\cos^2(\delta_\mu)\, \sin^2(\gamma_\mu) \;+\; \sin^2(\delta_\mu) \; , \end{aligned}$$

fulfilling $D^\mu_{11} + D^\mu_{22} = 2$.

Singlet-coupled APSG corresponds to all δ_μ in Eq. (6) being zero. The wavefunction model termed unrestriction in active pairs (UAP)[21] extends UHF in what makes the difference between Eqs.(5) and (6). The construction proposed by Rassolov is more general in allowing higher than two-dimensional geminal subspaces and considering geminal subspace dimensions subject to variation, in addition to orbitals and geminal coefficients[22]. The UAP geminal can be represented on the basis of paired orbitals ϕ and χ too, as discussed in Ref.[21]. When approaching from this angle, UAP geminal μ involves that particular virtual orbital of the beta set, which is paired with the occupied ϕ_μ in the sense of Karadakov[73, 74], and the same holds for χ_μ and the virtual alpha set.

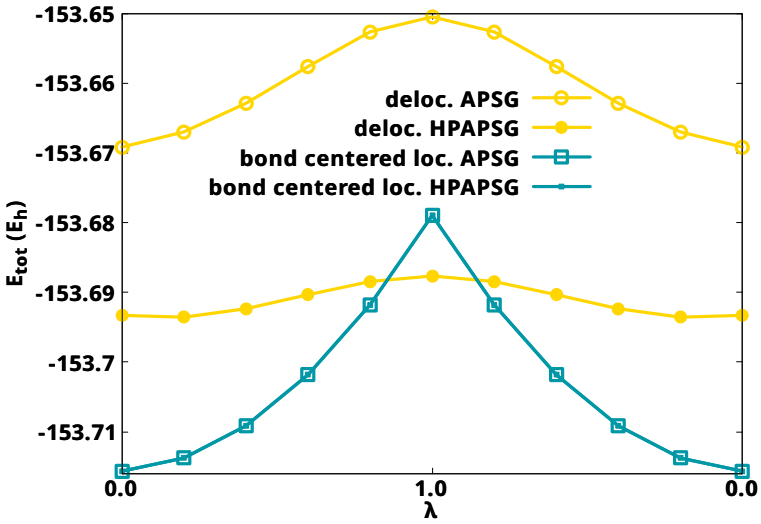


Figure 1: *Total energy of the C_4H_4 molecule by geminal based wavefunction models in cc-pVDZ basis, along a rectangle to square transformation. Reaction coordinate, λ interpolates $d(CC)$ bond distances between the minimal energy rectangular ($\lambda = 0$) and square ($\lambda = 1$) values, obtained at the multireference average quadratic coupled-cluster level of theory[75]. Bond lengths $d(CH)$ and angles $\angle(H, C, C)$ are fixed from the rectangular structure. Hollow symbols are used for singlet-coupled APSG energies, obtained by the Ansatz of Eqs.(1), (2) and (6). Filled symbols are used for the partially spin-purified HPAPSG, given by Eq. (9), vide infra. All geminal models are fully optimized, including geminal coefficients and orbitals. Distinct solutions of parameter optimization are indicated by different color and illustrated in Fig. 2 for the square structure.*

A key aspect of the spin-unrestricted SO geminal model is that the characteristic cusp on perfect pairing energy profiles accompanying the switch between Lewis-structures can be rectified within the framework of the single geminal product Ansatz of Eq. (1). A prototype situation is shown in Fig. 1 taking the distortion of the cyclobutadiene molecule around the D_{4h} structure as an example. The energy profile of the singlet-coupled Ansatz (hollow square symbol) is non-differentiable at the fourfold symmetric arrangement ($\lambda = 1.0$), as the energy curves corresponding to the

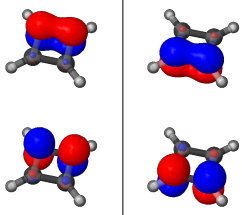
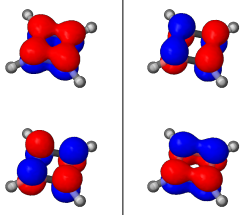
μ	1	2
bond centered localized orbitals		
$\gamma_\mu/^o$, APSG $\delta_\mu/^o$, APSG	14.8 0.0	14.8 0.0
$\gamma_\mu/^o$, HPAPSG $\delta_\mu/^o$, HPAPSG	14.8 0.3	14.8 17.9
delocalized orbitals		
$\gamma_\mu/^o$, APSG $\delta_\mu/^o$, APSG	3.0 0.0	45.0 0.0
$\gamma_\mu/^o$, HPAPSG $\delta_\mu/^o$, HPAPSG	5.1 59.0	45.0 10.1

Figure 2: *Optimized orbitals of geminals $\mu = 1, 2$, describing the π-system of the C_4H_4 molecule at the D_{4h} structure in cc-pVDZ basis. Bond lengths $d(CC) = 1.461$ Å and $d(CH) = 1.093$ Å are optimized at the multireference average quadratic coupled-cluster level of theory[75]. The two orbital sets correspond to distinct minima in the parameter space. Optimal orbitals of APSG and HPAPSG are not the same, but would not be discernible on the plot. Angles γ_μ and δ_μ parametrize the geminal coefficient matrix according to Eq. (6). See Fig. 1 for energetics and acronyms.*

two Kekulé structures exhibit a nonzero derivative of opposite sign at $\lambda = 1.0$. Optimal orbitals underlying the lowest energy singlet-coupled solution can be attributed to carbon-carbon π-bonds, as reflected by the top panel of Fig. 2, labeled "bond centered localized orbitals". The bias of singlet coupling for localized electron pairs is also apparent in Fig. 1, where the delocalized orbitals' APSG curve (hollow circle symbol) can be seen to lie some $30 - 45$ mE$_h$ above the curve with localized orbitals. Though the APSG solution with delocalized orbitals (c.f. bottom panel of Fig. 2) is free from the erratic cusp feature at $\lambda = 1.0$, it represents a local minimum in the parameter space.

Of the two APSG solutions in Fig. 1, one is triplet unstable at $\lambda = 1.0$, the other is not. This means that allowing parameters δ_μ to become nonzero, no distinct solution is found with localized orbitals, while the energy is lowered with delocalized orbitals, getting below the global minimum singlet-coupled APSG at $\lambda = 1.0$, to a value of

-153.691880 E_h. The global minimum UAP curve (not shown in Fig. 1) is accordingly well behaving at $\lambda = 1.0$, thanks to the delocalized character of the underlying orbitals. The considerable energy gain by UAP is accompanied by significant spin-contamination, producing $\langle \hat{S}^2 \rangle = 1.22$ at $\lambda = 1.0$, almost halfway between pure singlet a triplet. The energy of the UAP solution stays below singlet-coupled APSG in a relatively narrow interval around $\lambda = 1.0$, where the system shows strong biradical character, for which the singlet-coupled, localized bonds based description is obviously inadequate.

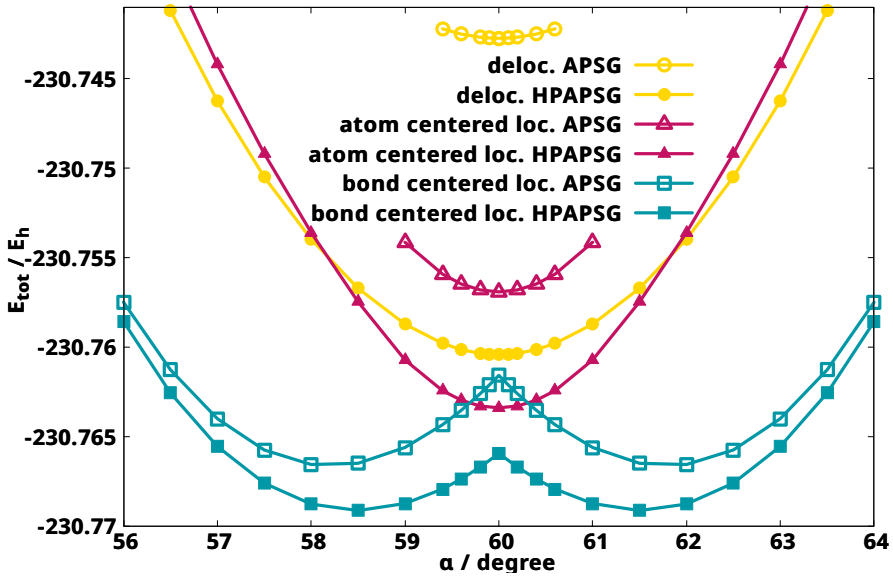


Figure 3: *Total energy of the C_6H_6 molecule by geminal based wavefunction models in cc-pVDZ basis, with carbon atoms positioned on a circle of radius* 1.4096 *Å . Inner angle of CC units, measured at the center follow the alternating pattern of* α, $120 - \alpha$, ..., *in degrees. Hexagonal symmetry corresponds to* $\alpha = 60°$. *Molecular structure at* $\alpha \neq 60°$ *is a* D_{3h} *distorted hexagon. Bond distance* $d(CH) = 1.0968$ *Å is optimized for the hexagonal structure at the CCSD(T) level of theory. See legend of Fig. 1 for acronyms. All geminal models are fully optimized, including geminal coefficients and orbitals. Distinct solutions of parameter optimization are indicated by different color and illustrated in Fig. 4 for the hexagonal structure.*

Examining a similar distortion of the aromatic benzene molecule, around D_{6h} to D_{3h} structure, one again finds a cusp on the singlet-coupled APSG curve, with orbitals localized between neighbouring carbon atoms. This is seen at $\alpha = 60°$ in Fig. 3 and in the top panel of Fig. 4. With geminals corresponding to carbon-carbon π-bonds, Kekulé structures are favoured energetically (around $\alpha = 58°$ and $62°$) and the hexagon is predicted to be a local maximum. Alternative stationary solutions of orbital optimization correct these qualitative defects. Curiously, apart from the delocalized orbitals' curve (hollow circle symbol in Fig. 3, bottom panel in Fig. 4) we find an atom centered localized orbital set too (hollow triangle symbol in Fig. 3, middle panel in Fig. 4), both predicting the hexagonal structure as equilibrium but representing local

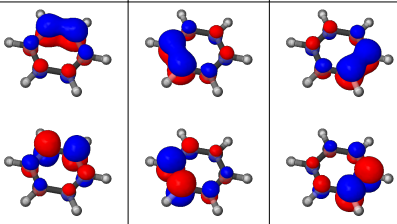
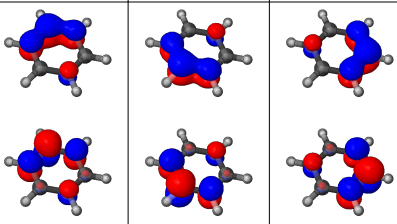
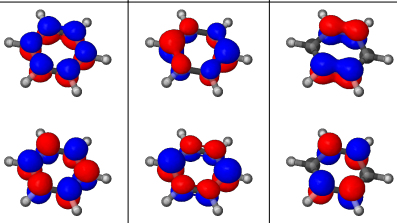
μ	1	2	3
bond centered localized orbitals			
$\gamma_\mu/^o$, APSG	8.6	8.6	8.6
$\delta_\mu/^o$, APSG	0.0	0.0	0.0
$\gamma_\mu/^o$, HPAPSG	8.5	8.5	8.5
$\delta_\mu/^o$, HPAPSG	13.8	13.8	13.8
atom centered localized orbitals			
$\gamma_\mu/^o$, APSG	7.4	7.4	7.4
$\delta_\mu/^o$, APSG	0.0	0.0	0.0
$\gamma_\mu/^o$, HPAPSG	7.8	7.8	7.8
$\delta_\mu/^o$, HPAPSG	14.9	14.9	14.9
delocalized orbitals			
$\gamma_\mu/^o$, APSG	1.5	8.7	7.9
$\delta_\mu/^o$, APSG	0.0	0.0	0.0
$\gamma_\mu/^o$, HPAPSG	3.0	9.6	9.2
$\delta_\mu/^o$, HPAPSG	14.6	21.2	21.4

Figure 4: *Optimized orbitals of geminals $\mu = 1, 2, 3$, describing the π-system of the C_6H_6 molecule at the D_{6h} structure in cc-pVDZ basis. Bond lengths $d(CC) = 1.4096$ Å and $d(CH) = 1.0968$ Å are optimized at the CCSD(T) level of theory. The three orbital sets correspond to distinct minima in the parameter space. Optimal orbitals of APSG and HPAPSG are not the same, but would not be discernible on the plot. Angles γ_μ and δ_μ parametrize the geminal coefficient matrix according to Eq. (6). See Fig. 3 for energetics and acronyms.*

minima in the parameter space, in line with the case of cyclobutadiene. A marked difference with the cyclobutadiene example though is that neither of the singlet-coupled solutions are triplet unstable. Energy is not lowered by allowing parameters δ_μ to be-

come nonzero, geminal unrestriction does not bring about a distinct UAP solution for hexagonal benzene.

Breaking multiple covalent bonds is a further example where the shortcomings of the singlet-coupled SO geminal Ansatz manifest[6, 76]. Spins recouple during the process starting from singlet bonding pairs and ending in non-singlet fragments with possibly unpaired electrons. This induces triplet instability, the UAP solution appearing at some point along the reaction coordinate, an analogue of the Coulson-Fischer point[77] in the geminal framework. We followed several dissociation processes in Ref.[50], monitoring fragment spin in addition to energy, which nicely showcases the improvement of UAP over singlet-coupled APSG in the dissociation limit.

5 Restoring spin symmetry

Gaining energy at the expense of spin-contamination raises the symmetry-dilemma articulated by Löwdin at the HF level[78]. When energetics of the system is of prime interest, a slight spin-violation is often acceptable. When unrestriction is accompanied by significant spin-contamination, one escapes deficiencies of spin-restriction but obtains a wavefunction with sizable weights from two or more exact roots of different spin quantum number. This not only makes hard to identify which state of the system is approximated, but undermines property calculations and correction schemes built upon such a starting point. Problems with perturbation theory with a severely spin-contaminated zero-order function have been reported at the HF[79, 80] as well as geminal levels[49, 81].

Such cases call for restoration of spin symmetry, which is possible by Löwdin's projector[82, 83] or by applying the projector of the desired irreducible representation of the rotation group[84]. The latter route has been revived lately[85], as it avoids expansion of the projected function in the many-electron Hilbert-space, simplifying the evaluation of matrix elements considerably.

Spin-projection may be performed before or after variational optimization of wavefunction parameters. The latter is more simple but enhances non-analiticity of the potential energy surface at the point of instability where the spin-contaminated solution appears. Optimization of a spin-projected function may be cumbersome but instability points become less of a problem and are completely eliminated when spin-symmetry is fully restored. Unless stated otherwise, we are considering projected then varied schemes in the present report.

Irrespective of the method used for formulating the spin-projector, size-consistency violation (i.e. non-additivity of the energy over non-interacting subsystems) is an unavoidable side-effect. In Ref. [72] we provided a formal analysis of size-inconsistency for spin-projected, unrestricted Ansätze in parallel at the HF and SO geminal product level. The effect was traced to high-spin monomer wavefunction components coupling to zero dimer spin that give a nonvanishing contribution to the non-interacting dimer energy. Since high-spin monomer components are not contributing to the energy in the absence of the non-interacting partner, the dimer energy does not match twice the

monomer energy in general (typically the latter is lower).

Taking a broader look, the source of size-inconsistency upon spin-projection is that spin-coupling is described in a reduced parameter space. The effect is missing when geminal spins are coupled properly at the outset, since energy contributions of spin terms are associated with individual variational parameters and high-energy monomer contributions to the non-interacting dimer can vanish upon optimization. Reduced variational flexibility of spin-broken and projected schemes leave some consistency violating terms in the dimer. This also explains the difference in the consistency violation of spin-projected then varied extended HF (EHF) and its geminal counterpart, extended APSG (EAPSG).[3] While EAPSG is size-consistent for two non-interacting geminals, EHF is violating already at this level, which has to do with geminal parametrization of Eq. (6) allowing for a spin pure geminal, but Eq. (5) in general not. Size-inconsistency of EPASG starts to manifest at the level of two non-interacting four-electron units. Inconsistency could be pushed to an even higher level with spin-projection of a restricted pairing function, admitting proper spin-coupling of e.g. all geminal pairs, but not of higher clusters.

The above discussion also clarifies the reason of size-inconsistency and spin-violation being antagonistic phenomena in the spin-projected, unrestricted wavefunction class. As spin-coupling is restored by projection, high-spin monomer wavefunction terms are introduced which potentially spoil the non-interacting dimer energy as a consequence of the constrained parametrization of the unprojected function. It is not necessary to stick with one of the two extremes, i.e. size-consistent but spin-violating UHF or UAP and spin-pure but considerably size-inconsistent EHF or EAPSG. A variety of midway solutions are offered by partial spin-purification, proposed and tested mostly in the context of HF[86–89] but also in the geminal framework[90]. Our own interest turned into this direction when numerical characterization of size-inconsistency of the fully spin-projected, EAPSG model gave rather discouraging results.

Of the partial spin-restoration techniques we applied Smeyers' idea of half-projection (HP)[87, 91]. It follows the approach formulated by Löwdin, but keeps only two of the combinatorially many terms: the original one and its spin-flip counterpart. This can be easily achieved by applying the half-projector

$$\hat{P}_S = \frac{1}{2}\left(1 \; + \; (-1)^S \; \hat{\mathcal{P}}_{\rm sf}\right) \; , \tag{7}$$

where S decides on the parity of the desired spin quantum number. The effect of the spin-flip operator $\hat{\mathcal{P}}_{\rm sf}$ on an $M_S = 0$ determinant is evaluated as

$$\hat{\mathcal{P}}_{\rm sf} \; i^+_\beta \ldots j^+_\beta k^+_\alpha \ldots l^+_\alpha |{\rm vac}\rangle = k^+_\beta \ldots l^+_\beta i^+_\alpha \ldots j^+_\alpha |{\rm vac}\rangle \; . \tag{8}$$

The reason behind half-projection terminology is that roughly half of the contaminants are eradicated by the action of $\hat{P}_S$, namely those belonging to spin quantum number

[3]For notational simplicity we keep APSG for the singlet-coupled Ansatz when the acronym stands in itself, but admit the spin-unrestricted (i.e. nonzero δ_μ in Eq. (6)) case when preceded by a prefix e.g. 'E' or 'HP'.

of parity opposite to S[91]. The half-projected spin-unrestricted geminal product is obtained as

$$\Psi_{\mathrm{HPAPSG}} = \hat{P}_S \Psi \tag{9}$$

where Ψ is taken from Eq. (1). Similarly to EAPSG, variation is performed after projection in the HPAPSG model. Parameters are optimized based on the Brillouin-condition

$$\langle \delta\Psi_{\mathrm{HPAPSG}} \,|\, \hat{H} - E_{\mathrm{HPAPSG}} \,|\, \Psi_{\mathrm{HPAPSG}} \rangle = 0 \ , \tag{10}$$

with the HPAPSG energy obtained as the Rayleigh-quotient

$$E_{\mathrm{HPAPSG}} = \frac{\langle \Psi_{\mathrm{HPAPSG}} \,|\, \hat{H} \,|\, \Psi_{\mathrm{HPAPSG}} \rangle}{\langle \Psi_{\mathrm{HPAPSG}} \,|\, \Psi_{\mathrm{HPAPSG}} \rangle} \ . \tag{11}$$

In our initial studies only parameters in Eq. (6) were optimized and orbitals were conserved as UNOs[92]. In analogy with APSG and UAP, the HPAPSG optimization of parameters in Eq. (6) leads to the eigenvalue problem of an effective two-electron operator, providing geminals as eigenfunctions. An important consequence of half-projection is a coupling beyond mean-field in the expression of the HPAPSG effective geminal-operator.

Orbitals underlying the geminal coefficient matrix of Eq. (6) turn out to be natural orbitals at the HPAPSG level also. General expression of the spin-summed geminal density matrix can be found in Ref. [92], we suffice here with giving occupation number of orbitals φ_1 and φ_2 at the HPAPSG level

$$\begin{aligned} D^{\mu}_{11} &= \big\{ 2\cos^2(\delta_\mu)\,\cos^2(\gamma_\mu)(1 + f\mathcal{M}/\cos(2\delta_\mu)) \\ &+ \sin^2(\delta_\mu)(1 - f\mathcal{M}/\cos(2\delta_\mu)) \big\} \ / \ (1 + f\mathcal{M}) \ , \\ D^{\mu}_{22} &= \big\{ 2\cos^2(\delta_\mu)\,\sin^2(\gamma_\mu)(1 + f\mathcal{M}/\cos(2\delta_\mu)) \\ &+ \sin^2(\delta_\mu)(1 - f\mathcal{M}/\cos(2\delta_\mu)) \big\} \ / \ (1 + f\mathcal{M}) \ , \end{aligned}$$

with $f = (-1)^S$ and $\mathcal{M} = \prod_\mu \cos(2\delta_\mu)$. Comparing the above HPAPSG natural occupation numbers with the previously given UAP expressions, it is notable that not only parameters of geminal μ, but those of all others contribute to the occupation numbers of geminal μ, via quantity $\mathcal{M}$.

In Ref. [92] size-inconsistency was analysed both by formulae and in numerical terms on the smallest nontrivial example of the dimer of the two-geminals H_4 system. Full as well as half-projected data at the HF and geminal level indicate, that the magnitude of size-inconsistency mainly depends on the projection scheme, and shows less sensitivity to the level of sophistication of the unrestricted Ansatz. Numerical data support that inconsistency of HP schemes is smaller than full projection, though not by orders of magnitude. Note that size-inconsistency data of Ref. [72] have been corrected in Ref. [92].

Apart from size-consistency, we carried out a formal analysis of size-extensivity (i.e. the infinite limit of many identical units) revealing that the energetic effect of half-projection becomes gradually negligible in the thermodynamic limit. This result parallels early studies of projected unrestricted HF schemes[93, 94].

Optimization of orbitals at the HPAPSG level is not more costly than APSG, featuring an $\mathcal{O}(N_{\text{basis}}^5)$ scaling[95]. Orbital optimized HPAPSG data are shown on the reaction profiles in Figs. 1 and 3 with filled symbols. Examining the case of cyclobutadiene, energy improvement by intergeminal spin-coupling in HPAPSG is characteristically different with localized and delocalized geminals. The former potential curve is hardly affected by HP, even though a distinct solution is obtained, as demonstrated by nonzero δ_μ in Fig. 2. It is interesting to note the deviation of HPAPSG δ_1 and δ_2 with localized geminals, indicating spatial symmetry violation in addition to spin violation. With delocalized geminals, HPAPSG brings a cca. 20-40 mE_h improvement over APSG. The significance of the HPAPSG curve with delocalized orbitals in Fig. 1 (filled circle symbol) is that it represents the simplest SO geminals based approximation, giving a qualitatively correct approximation of the ground state. In particular it (i) is the global minimum around the square geometry (ii) features zero derivative and has a maximum at $\lambda = 1$ (iii) is only slightly spin-contaminated, $\langle \hat{S}^2 \rangle = 0.32$. Though the value of the square to rectangle transformation barrier is significantly underestimated by the delocalized orbitals' HPAPSG curve (around $12 - 15$ mE_h by benchmarks in the same basis[75, 96]), it serves as good reference for dynamical correlation treatment, vide infra.

Square cyclobutadiene is a good example to point out that the energy does not necessarily decrease with spin-projection followed by variation. The value of the HPAPSG energy at $\lambda = 1$ is -153.687662 E_h, roughly 4 mE_h higher than UAP at this geometry. An argument supporting the validity of this result is that the weight of all spin-components remaining after partial spin-projection are increased, not only that approximating the ground state but also those of the contaminants, possibly of high energy. The ordering of the HPAPSG and UAP energy is a result of an optimization balance. Though the HPAPSG energy often lies below the UAP energy, this is not necessary.

For the benzene molecule, intergeminal spin-coupling in HPAPSG lowers the energy of all three solutions shown in Fig. 3. The effect gets larger with growing delocalized character of the orbitals. In this case however, the qualitatively incorrect curve, with energy minima at Kekulé structures and cusp-shaped maximum at the hexagonal arrangement remains the global optimum even at the HPAPSG level. A dynamical correlation treatment should obviously rather be based on either of the HPAPSG solutions, giving a qualitatively correct energy profile.

6 Perturbative corrections

The strongly orthogonal geminal product function misses intergeminal correlation completely at the singlet-coupled level and the effect is recovered only marginally by unrestricted and projected versions of the Ansatz. A proper account of intergeminal dynamic correlation requires a perturbational or coupled cluster (CC) correction in multireference (MR) formalism, the geminal wave function serving a multi-determinantal reference.

When working out correlation correction schemes, the SO constraint of geminals again proves to be of enormous help in keeping derivations simple. The algebraic reason behind this is that, although the geminal creation operators of Eq.(2) do not exhibit a closed algebra[48, 97], their commutator (indicated by square brackets) is evaluated under SO as

$$\begin{aligned}
\left[\psi_\mu^+, \psi_\nu^+\right] &= 0 \\
\left[\psi_\mu^-, \psi_\nu^-\right] &= 0 \\
\left[\psi_\mu^-, \psi_\nu^+\right] &= \delta_{\mu\nu} \left(1 - \sum_{ij\in\mu} \left(\boldsymbol{C}^\mu \boldsymbol{C}^{\mu\dagger}\right)_{ij} \; \varphi_{i\alpha}^+ \varphi_{j\alpha}^- - \sum_{ij\in\mu} \left(\boldsymbol{C}^{\mu\dagger} \boldsymbol{C}^\mu\right)_{ij} \; \varphi_{j\beta}^+ \varphi_{i\beta}^- \right) ,
\end{aligned} \tag{12}$$

where adjoint geminal operators are defined as

$$\psi_\mu^- \; = \; \sum_{ij\in\mu} \; C_{ij}^{\mu *} \; \varphi_{j\beta}^- \varphi_{i\alpha}^- \; . \tag{13}$$

Note that in the absence of SO the Kronecker-delta in Eq. (12) would not be present[98]. Significance of $\delta_{\mu\nu}$ in Eq. (12) is that it ensures

$$\psi_\mu^- \; \psi_\nu^+ |\mathrm{vac}\rangle \; = \; \delta_{\mu\nu} \; |\mathrm{vac}\rangle \; , \tag{14}$$

thus the adjoint geminal operators ψ_μ^- of Eq. (13) can be considered as true annihilation operators. In that sense, SO geminals can be considered as composite Bose-like quasiparticles[48].

Dynamical correction schemes typically require many-body excitations of the reference, which can be represented with excited and ionized functions constructed in the original geminal subspaces. From this point the above simple algebraic properties are no longer valid, but systematization of the excited functions and computation of matrix elements is still simpler than with a general geminal reference. The key point is that orbitals φ_i remain localized in the associated geminal subspace, which represents an enormous computational simplification.

Considerations are further simplified if allowing two spatial orbitals at maximum per geminal subspace, c.f. the wavefunction historically called generalized valence bond (GVB)[99]. The GVB reference has been a popular starting point of dynamic correlation treatments by MR perturbation theory (PT)[100–102], CC[19, 103, 104], configuration interaction[105] and less conventional schemes[106–108].

Perturbation methods exploiting the geminal structure of APSG were pioneered by Surján[9–11]. Ref. [12] represents a culmination of the singlet-coupled APSG based developments, giving a pictorial representation of geminal subspace based categorization of excited functions needed to construct the first order wavefunction. An important feature is the formulation of the zero-order with effective geminal Hamiltonian operators, including explicit intrageminal Coulomb-interaction. The partitioning is therefore of Dyall-type[109], which typically promotes superior performance over one-body zero-order operator based PTs. Tractability of the first-order equations is ensured by the

sum-over-geminals form of the zero order Hamiltonian together with the product-over-geminal subspaces construction of the excited functions. Closely related, APSG based PT frameworks were designated by Rassolov and coworkers[53] and Xu and Li[110].

Correlation schemes based on singlet-coupled APSG obviously break down, when triplet geminals are essential for static correlation. Taking the multiple covalent bond breaking scenario, the problem technically manifests in singlet and triplet geminals becoming degenerate for the dissociating electron pairs, which contribute a PT denominator tending to zero in the separated fragments limit. An immediate remedy is to incorporate triplet states of geminals in question coupled properly to singlet at the level of reference, as demonstrated for the case of H_2O symmetric dissociation in Ref. [49]. Clearly, all affected geminals are to be considered in the general case, which would take to a VB-type approach mentioned at the beginning of Section 4.

A straightforward extension of the geminal based, Dyall-partitioning bolstered PT for the unrestricted geminal product reference was reported in Ref. [81]. Orbital optimization not being available in our code at the time, we sticked with UNOs and decided on active (i.e. non HF) geminals by setting a threshold on UNO occupation numbers. This procedure, following in the footsteps of Pulay's UNO-CAS[111], is justified by the close relation between UHF and UAP, vide supra. Black-box computation of a minimalistic geminal product type reference is an associated advantage (note that geminal subspace dimensions are limited at 2 in UHF), keeping us applying this approach whenever the restricted HF reference shows triplet instability. Finding UHF solutions is assisted by a recently devised algorithm of Tóth and Pulay[112]. Triplet state of geminals being incorporated at the level of reference, low-lying excited states affording a geminal based description are natural target systems of unrestricted geminals' based PT. We reported excellent performance on singlet-triplet splitting of several biradical systems by geminal PT based on UHF in Ref. [81], with slight spin-contamination. Serious spin-contamination however led to spectacular failure in complete analogy to unrestricted Møller-Plesset with strong spin-contamination of the reference[79, 80].

An evident cure to the problem is starting the perturbation procedure from the spin-purified geminal product, which can be done in two essentially different ways. Taking the spin-purified wavefunction, e.g. Eq. (9) as zero-order function, the Dyall-type, sum-over-effective geminal Hamiltonians zero-order is to be abandoned. This is because spin-projection results in a sum of multiple geminal product terms in general, which can not be an eigenfunction of such an operator. Alternatively, one may insist on using effective geminal Hamiltonians in the zero-order operator, and accept that its eigenfunction, i.e. the zero-order solution is the spin-contaminated, single geminal product of the form of Eq. (1). The former route was taken by Tsuchimochi and Ten-no at the HF level[113], and in our laboratory at the geminal level[114], with applying a tailor-made zero-order Hamiltonian. The latter option is reminiscent of symmetry-adapted perturbation theory (SAPT) developed in connection with weak intermolecular interactions by the Polish school[115] for ensuring antisymmetry over interacting fragments at finite orders of PT[116, 117]. Perturbative correction schemes devised by Handy and Knowles[118] and Tsuchimochi and Van Voorhis[119] can be considered an adaptation of SAPT for spin-projection at the HF level.

Working at the geminal level, we applied SAPT for half-projection considering weak[120] and strong[121] symmetry forcing schemes. Furthermore, several sophisticated options for the zero-order Hamiltonian were designed and tested to avoid intruder states and ensure that the formalism falls back to the comparatively straightforward, APSG based geminal PT framework in the spin-pure limit. First results on diradical systems, obtained on the basis of UNOs, nicely corrected on previous pathological cases[122]. The effect of orbital optimization was investigated in a second work[95]. Results collected in Table 1 for the vertical singlet-triplet gap of square cyclobutadiene indicate, that the effect of orbital optimization is rather negligible, emphasizing the advantages of using UNOs, as advocated by Pulay. The method of symmetry forcing at finite orders of the PT series on the other hand appears crucial.

Table 1: *Vertical singlet-triplet gap, $\Delta E = E_{triplet} - E_{singlet}$ of square cyclobutadiene computed in cc-pVDZ basis. See Fig. 2 for geometry. Benchmarks CIPSI+PT2 and CCSDT are taken from Ref. [96]. Acronym HPAPSG-SAPT2 refers to partitioning option 3 of Ref. [122], 'weak' and 'strong' designate the symmetry forcing scheme. Letter U in parentheses refers to orbitals being UNOs. Orbitals are optimized at the HPAPSG level, when '(U)' is missing from the acronym.*

	ΔE/mE$_h$
HPAPSG(U)-SAPT2, weak	12.6
HPAPSG-SAPT2, weak	12.7
HPAPSG(U)-SAPT2, strong	8.4
HPAPSG-SAPT2, strong	7.5
CCSDT	7.6
CIPSI+PT2	9.5

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